A new type of low power thermoelectric micro-generator fabricated by nanowire array thermoelectric material

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Abstract

A new type of thermoelectric micro-generator, which is composed of n-type and p-type Bi_2Te_3 nanowire array thermoelectric materials, is designed to be energy source for miniaturized solid-state devices such as MEMS, micro-electrical system and even "system on a chip". The nanowire arrays are fabricated by electrochemical deposition of Bi_2Te_3 into the nano-pores of alumina template. The measurements showed that the Seebeck coefficient α of p-type and n-type Bi_2Te_3 nanowire arrays is about 260 and -188 $\mu V/K$ separately with the nanowire diameter of about 50 nm at 307 K. The thermoelectric micro-generator is designed to possess a film like configuration and a laminar structure as C layer/B layer/A layer/B layer/C layer. The A layer is thermoelectric material layer consisting of a great amount of n-type and p-type nanowire micro-zones. Two B layers are electric conductive layers which realize the series electric connection of n-type and p-type micro-zones in A layer. The other two C layers are thermal conductive layers. By the use of IC technology, the micro-generator can obtain a high voltage output, and its thickness is less than 200 μm. The unique laminar structure makes thermo-electricity conversion more effective. An important aspect that distinguishes our device from the conventional one is that thermoelectric nanowire arrays are firstly used to fabricate thermoelectric micro-generator.
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1. Introduction

The development of micro-electromechanical system (MEMS) based on micro-machining and microelectronics technologies has been significant recently and widened the application of miniature sensors and actuators [1]. For these micro-systems, it is difficult to be supplied with power due to the large size and limited service life of conventional battery. So, it is of great importance to prepare new micro-device as power supplier to meet the requirement of MEMS. Of the renewable power

sources, low power thermoelectric micro-generator is a promising candidate as it can convert the heat into electricity under temperature gradient condition and shows reliable performance and long life. Latest advancement in preparing new thermoelectric materials with good performance has made it available to fabricate feasible micro-generator. Furthermore, with the help of microelectronic technology in IC fabrication process, thermoelectric power generator can be made in smaller size and yield higher voltage output [2]. Nevertheless, the efficiency of the bulk thermoelectric material is still very low. Until present, the reported researches about thermoelectric micro-generators have been focusing on miniaturizing n-legs and p-legs in the micro-devices and the smallest size has already reached micrometer scale. But the properties of the thermoelectric material used in this form are almost the same as that in bulk. It has been verified by theory and experiments that the nanowires of thermoelectric material should have an enhanced figure of merit due to the quantum-size effects [3,4]. Among them, Bismuth and its compounds are most promising at low temperature range. In our lab, one-dimensional n-type and p-type Bi_2Te_3 nanowire arrays have been successfully prepared by electrochemical deposition (ECD) technology with porous alumina film as template. Based on those work, a new type of thermoelectric micro-generator comprised of n-type and p-type nanowire array has been designed. This micro-generator can be used as not only an independent power generator, but also can be integrated with electric components together to convert waste heat into electric power.

2. Preparation and characterization of Bi_2Te_3 thermoelectric nanowire array

The thermoelectric conversion efficiency is determined by the figure of merit ZT. $Z = \alpha^2 \sigma / \kappa$ where α, σ and κ are the Seebeck coefficient, electric conductivity and thermal conductivity respectively. It can be seen that ZT is concerned with α, σ and κ. Researches indicate that α, σ and κ are not independent mutually, they are all the function of carrier density. The conventional dop-

ing method can not improve the thermoelectric performance of semiconductor efficiently for it will cause the simultaneous changes of α, σ and κ. Currently, the best ZT value of commercial bulk doping semiconductor for $Bi_{2(1-x)}Sb_{2x}Te_3$ compound is about 1 at room temperature, and its thermoelectric conversion coefficiency is less than 5%. It has been verified theoretically recently that the values of α, σ and κ depend on the width of quantum well. So the value of ZT can be improved greatly by decreasing the dimension of thermoelectric material to nano-scale [5,6]. The theoretical analyses by quantum-mechanics have indicated that the value ZT of one-dimensional nanowire thermoelectric materials can be improved greatly, and this has been proved by experiment recently [7]. In our Laboratory, nanowire array thermoelectric materials have been electrochemically assembled by electrodepositing elements bismuth and tellurium into the nano-pores of alumina template [8–10].

The surface morphology (PHILIPS XL30 ESEM) of porous alumina templates fabricated in our lab is shown in Fig. 1. A thin nickel film was deposited onto one side of the alumina template by PVD as a conductive layer. In a three electrode system with the alumina template as working electrodes, Pt plate as auxiliary electrode and saturated calomel electrode (SCE) as reference electrode, n-type and p-type Bi_2Te_3 nanowires were potentiastatically electrodeposited
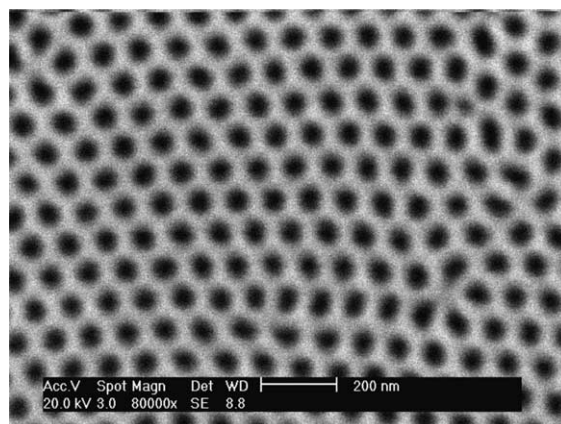

Fig. 1. Surface ESEM morphology of porous alumina template.

Table 1
Composition of the electrodeposition solution

Composition	Concentration (M)
NO_3^{1-}	1
Bi^{3+}	0.013
$HTeO_2^+$	0.010

into the nanopores of alumina templates at the potential of −0.10 V (vs. SCE) and −0.15 V (vs. SCE) respectively in the same solution listed in Table 1. A potentiostat (TD3690) was used to realize the potentiostatic control. All the processes were carried out under an inert atmosphere (nitrogen). The Bi_2Te_3 nanowire arrays prepared under the condition mentioned above were immersed in NaOH solution to remove the alumina template. Then the nanowires were taken out by Cu meshwork for TEM analysis

(PHILIPS TECNAI20 TEM). The morphology of the nanowires are shown in Fig. 2(a) and their diameter is about 50 nm. Fig. 2(b) is the sectional ESEM morphology of the nanowire arrays. It can be seen that Bi_2Te_3 nanowires are embedded in the alumina base and its thickness is about 100 μm. The bottom of nanowires is connected through Ni layer and the top of nanowires is collected together on the surface of template. The seeback coefficients of prepared n-type and p-type Bi_2Te_3 nanowire array were measured on the two sides of template in room temperature range and the results are shown in Fig. 3. Since all the nanowires are connected in parallel, the seeback coefficients of nanowires can be obtained by measuring a small area of the sample. It can be found that the seeback coefficients of n-type and p-type Bi_2Te_3 nanowire arrays at room temperature are about 270 and −188 μV/K
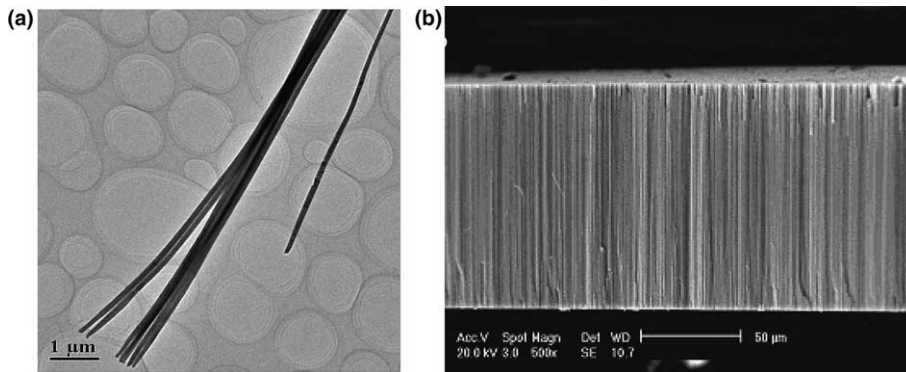

Fig. 2. (a)TEM morphology of nanowires. (b) Cross-sectional view of ESEM image of Bi_2Te_3 nanowires assembled in the alumina template.
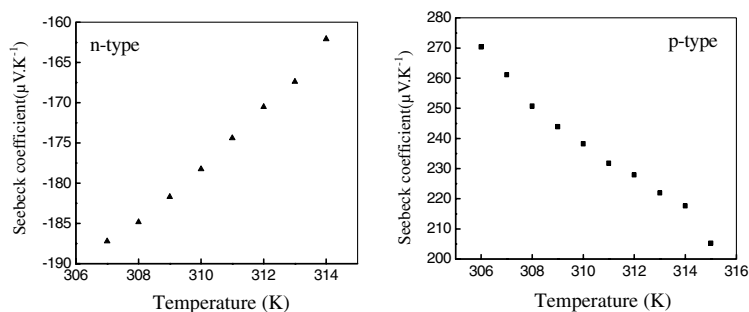

Fig. 3. Seebeck coefficient–temperature relations of electrochemically assembled n-type and p-type Bi_2Te_3 nanowire array.

separately, which is a little bigger than that of bulk Bi_2Te_3 materials at same temperature range. The α value of the Bi_2Te_3 nanowire arrays is not as high as expected. The wires' diameter of about 50 nm maybe too large to expect an obvious improvement of the thermoelectric properties. Focusing on another aspect, the composition of the Bi_2Te_3 nanowires may not be the best. The behavior of the Seebeck coefficient α is related to the carrier concentration. Changing the concentration of the electrolyte and adjusting the electrodeposition potential may optimize the doping extent of the Bi_2Te_3 nanowires to improve the thermoelectric power.

3. Design of the thermoelectric micro-generator

After the successful preparation of n-type and p-type Bi_2Te_3 nanowire array thermoelectric materials, the following problem is how to connect electrically the nanowires in series to make a thermoelectric micro-generator. Clearly, it is easy to connect electrically all the nanowires in the nanowire array in parallel, simply by covering the both surfaces of the nanowire array with conductive layers. However, to obtain a high voltage output, the nanowires in the nanowire array must be connected in series. If the nanowires are connected in series one by one, it is almost impossible with present technology for the high density of nanowires that is over 10^9 n/cm². Even if this can be realized, it will bring a huge internal resistance and decrease the output power a lot and even make the micro-generator less useful. Here, we propose a feasible structural design for the thermoelectric micro-generator composed of nanowire array thermoelectric material. The new thermoelectric micro-generator is designed to possess a laminar structure as C layer/B layer/A layer/B layer/C layer.

In this structure, A layer is composed of a large amount of p-type and n-type nanowire array thermoelectric material micro-zones in equal numbers, and each micro-zone is separated by alumina to realize insulative contact among them. Fig. 4(a) is the structural schematic view of A layer. B layer (Fig. 4(b)) is electric conductive layer which realizes the electric connection of the n-type and p-type micro-zones of A layer in series. C layer acts as thermal conductive and encapsulation layer. The size of n-type and p-type micro-zones can be fabricated very small and the numbers of n-type and p-type micro-zones electri-
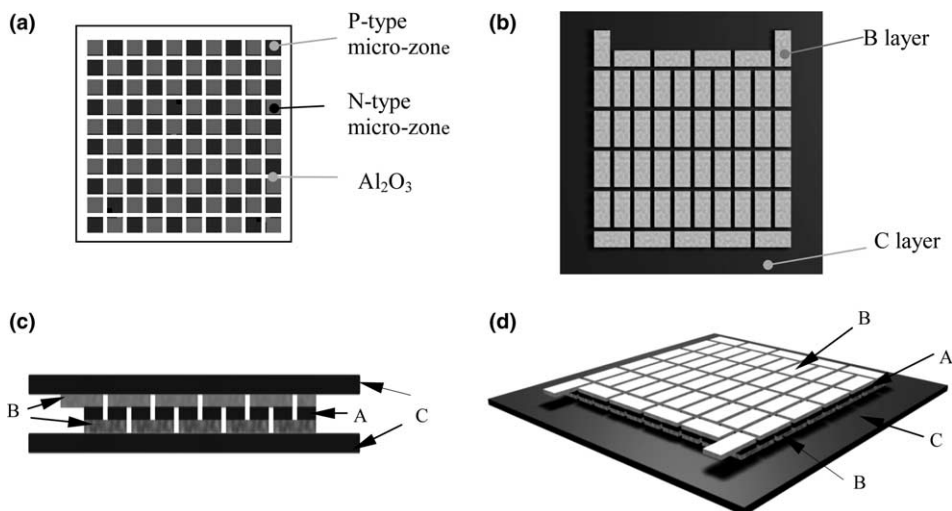

Fig. 4. (a) Structural schematic view of A layer. (b) Structural schematic view of upper conductive B layer and C layer. (c) Structural schematic elevation of thermoelectric micro-generator. (d) 3D structural schematic view of thermoelectric micro-generator (the upper C layer is omitted).

cally connected in series in A layer can be over millions in a small area less than 1 cm^2. So the film-like new thermoelectric micro-generator module can ensure a high voltage output with a thickness less than 200 μm and a small surface area. The structural schematic elevation of the new thermoelectric micro-generator module is shown in Fig. 4(c). Fig. 4(d) is its 3D structural schematic view. These figures are only used to schematically describe the structure of the thermoelectric micro-generator, so the numbers of the micro-zones are very limited.

4. Description of the fabrication process

A schematic process to fabricate the new type of thermoelectric micro-generator is shown in Fig. 5.

The fabricating process can be described as three parts: the fabrication of A layer, B layer and C layer. Nano-porous alumina film is used as template(a) and still keeps its barrier layer, which plays a very important role in this whole process. Au layer (about 2 μm thickness) is sputtered onto pores-open side of the alumina template to serve as a conductive layer on which the nanowires grow (b). Photoresist (BN 302-60) was spin coated onto the barrier layer of the alumina template to pattern the n-type micro-zones in which n-type thermoelectric nanowires will be deposited later. After the development and fixation of photoresist (c), the template was dipped into 5 wt% NaOH solution to open the nano-pores and fixed to an apparatus filled with ECD solution. The ECD of n-type Bi_2Te_3 in the patterned n-type micro-zones was conducted for 5 h, and n-type nanowire array
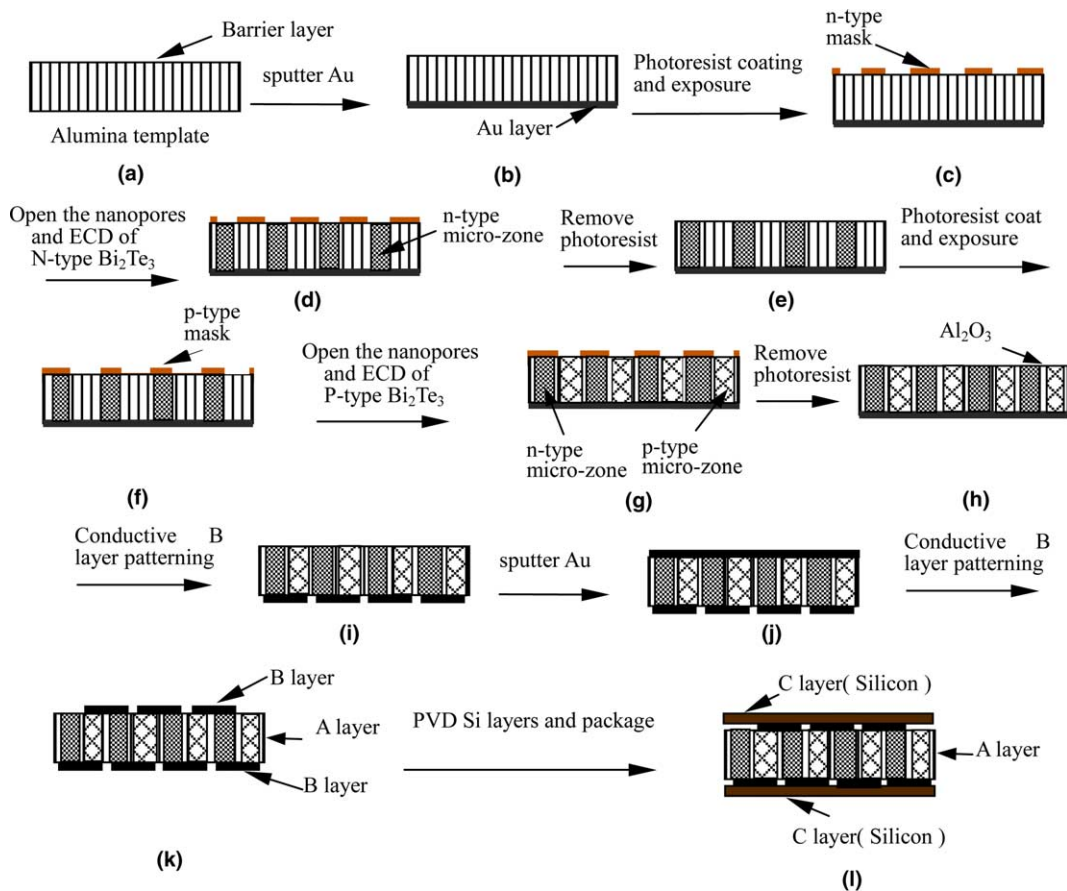

Fig. 5. Schematic process of fabricating thermoelectric micro-generator.

micro-zones were formed (d). After removing the remained photoresist, the template was spin coated again with the same photoresist and another mask was used to pattern p-type micro-zones in which p-type thermoelectric nanowire will be deposited ((e) → (f)). The same methods used for the ECD of n-type nanowire array would be used for the fabrication of p-type Bi_2Te_3 nanowire array micro-zones (g) and the A layer will be formed (h). The step i shows the fabrication of B layer directly by etching Au layer to realize the conductive connection of p-type and n-type micro-zones in one side of A layer. Another side of A layer will be coated again with Au layer (about 1 μm thickness) (j). Similarly, the Au layer will be patterned to connect the p-type and n-type micro-zones of A layer in series (k). Finally, Si will be deposited onto the surface of B layers to serve as thermal conductive layers.

Although the process has been designed, there is a long way to reach the final assemble. Fig. 6 is the fabricated n-type nanowire array micro-zones and the grey square areas are the top of nanowires collected in the microzones. The dimension of each micro-zone is 50×50 μm and internal space is left for the next step of ECD p-type nanowire. Fig. 7 is the cross-sectional view of the fabricated n-type nanowire array micro-zones. Because the thickness of the alumina template is considerable very large compared with the nanopore size, it is difficult to ensure the deposited thermoelectrical materials in
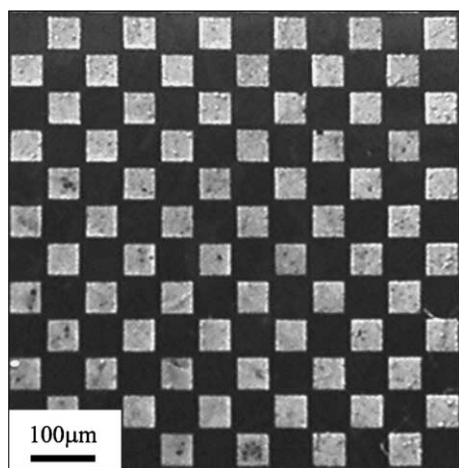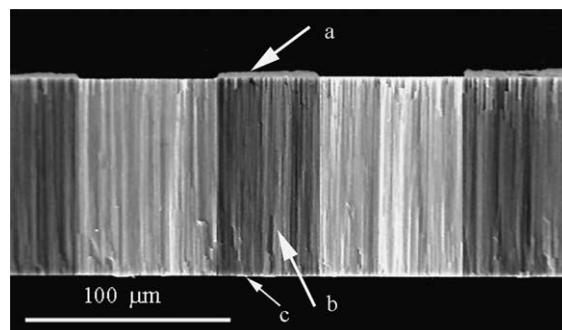

Fig. 7. Cross-sectional view of the n-type nanowire array micro-zones: (a) nanowires grew out of pores and collected on top of micro-zone; (b) thermoelectric material filled in the nanopores; (c) sputtered Au layer.

every nanopore to reach the surface of template at the same time. When the nanowires grow in the pores, their deposition rates are limited by the diffusion of metal ions into the pores. If any single nanowire grew to the surface firstly, the deposition rate will increase quickly because the diffusion of ions is not a problem. This will lead to the mushroom growth of the nanowire and its cover of neighbouring pores. Therefore, a certain amount of nanowires cannot grow up completely to the top of the template and resulted in considerable high resistance of one single micro-zone. During the experiment, we found that the filling ratio of the nanowires in the nanopores that can extend to the top of the template highly correlates with the structural uniformity of the templates, the ionic concentration of Bi^{3+} and $HTeO_2^+$ in the solution and the depositing rate. Our further study will focus on improving the filling ratio of nanowires in the nanopores.

It should be pointed out that the barrier layer of alumina film serves as a naturally protective cover of the pores. It keeps the fresh pores from being filled with photoresist and can be removed easily before the ECD of Bi_2Te_3. Since the alumina template itself is a kind of good insulting material, various metals can be deposited into the pores and electric connection can be realized on the surface of the template by the lithophotography and etching treatment. This fabrication method would make it possible to realize the fabrication of MEMS with nanowires.

Fig. 6. ECD of n-type nanowire array micro-zones.

Acknowledgments

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